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# All-Round Robustness of the Mn<sub>19</sub> Coordination Cluster System: Experimental Validation of a Theoretical Prediction

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Experimental and theoretical studies indicate that achieving the maximum possible ground spin state of  $S_T = 83/2$  for the mixed-valent Mn<sub>19</sub> coordination cluster is insensitive to replacement of its eight  $\mu_3$ -N<sub>3</sub> ligands by  $\mu_3$ -Cl,  $\mu_3$ -Br,  $\mu_3$ -OH or  $\mu_3$ -OMe, substantiating that the ferromagnetic interactions are indeed mediated mainly by the internal ( $\mu_4$ -O) ligands. The robustness of the inorganic {Mn<sup>III</sup><sub>12</sub>Mn<sup>II</sup><sub>7</sub>( $\mu_4$ -O)<sub>8</sub>} core is clear from the molecular structure and ESI-MS studies have shown that the structure of the Mn<sub>19</sub> aggregate, and also of its Mn<sub>18</sub>Y analogue, are stable beyond the solid state.

Recent years have witnessed an explosion of interest in producing cooperatively coupled molecular-based coordination clusters, CCs, and such CCs can be regarded as possessing inorganic cores of interacting metal ions contained within a shell of ligand species. Of particular interest is the case of CCs which are molecular magnets and an area of particular interest here is the idea of using ligand shell modification in order to provide systems which might, for example, be grafted onto various substrates. This idea has been recently illustrated with the successful attachment of modified Fe<sub>4</sub> Single-Molecule Magnets onto either metal surfaces or carbon nanotubes.<sup>1</sup> Requirements of such studies are (a) that the magnetic properties of the cluster are insensitive to such functionalisation and (b) that the system remains stable outside of the solid-state where the magnetic and other physical characterisation studies traditionally take place.

In our previous report on the Mn<sub>19</sub> aggregate [Mn<sup>III</sup><sub>12</sub>Mn<sup>II</sup><sub>7</sub>( $\mu_4$ -O)<sub>8</sub>( $\mu_3$ N<sub>3</sub>)<sub>8</sub>(HL<sup>Me</sup>)<sub>12</sub>(MeCN)<sub>6</sub>]Cl<sub>2</sub>·10MeOH·MeCN (**1**) (Fig. S1, H<sub>3</sub>L<sup>Me</sup> = 6-bis(hydroxymethyl)-4-methylphenol) we postulated that the ferromagnetic interactions within this compound that resulted in the  $S = 83/2$  spin ground state were largely mediated by the end-on ( $\mu_3$ -N<sub>3</sub>) ligands, rather than the ( $\mu_4$ -O)<sup>2</sup> ligands.<sup>2</sup> This followed the received wisdom of the time,<sup>3</sup> but subsequent DFT calculations suggested that in fact the oxido ligands within the inorganic {Mn<sup>III</sup><sub>12</sub>Mn<sup>II</sup><sub>7</sub>( $\mu_4$ -O)<sub>8</sub>} core play a decisive and dominant role in mediating these interactions.<sup>4</sup> This suggestion led us to consider the nature of this coordination cluster further and to the idea that the key to the structural topology,<sup>5</sup> and thus magnetic behaviour, might lie in the invariance of the inorganic {Mn<sup>III</sup><sub>12</sub>Mn<sup>II</sup><sub>7</sub>( $\mu_4$ -O)<sub>8</sub>} structure and that the encapsulating ligands do not affect the electronic structure of this core to any significant extent.

These suggestion are supported by the fact that, for example, we recently reported that replacing the 4-methyl substituent of the phenolic ligand by a methoxy group (H<sub>3</sub>L<sup>OMe</sup>) had very little effect on the magnetic properties of the Mn<sub>19</sub> aggregate.<sup>6</sup> Although we have shown that in other systems changing

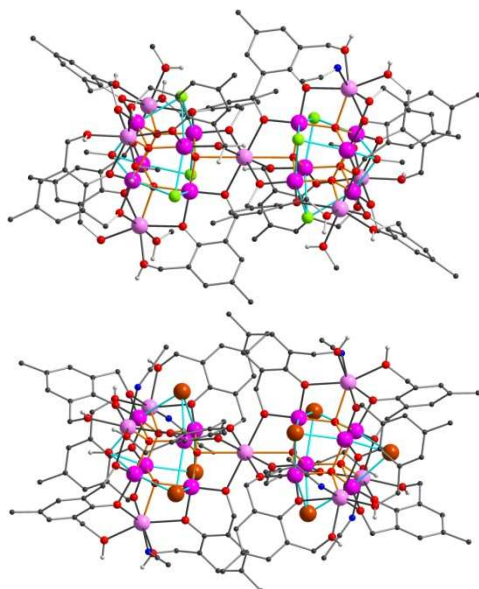
substitutions on the organic encapsulating ligands can have very significant effects on the molecular-based magnetic behaviour of the resulting coordination cluster,<sup>7</sup> it appears in this case that having a very strongly ferromagnetically coupled inorganic {Mn<sup>III</sup><sub>12</sub>Mn<sup>II</sup><sub>7</sub>( $\mu_4$ -O)<sub>8</sub>} core in the Mn<sub>19</sub> systems provides a truly robust unit for further decoration via the encapsulating ligands. This situation is of relevance when considering the possibility of tethering the cluster to a surface. Thus, in order to test the theoretical prediction<sup>4</sup> that the main mediators of the ferromagnetic coupling in the supertetrahedral subunits of **1** are the internal inorganic core-based oxido bridges rather than the external face-capping azide ligands, we set out to synthesise Mn<sub>19</sub> analogues in which azide salts are deliberately omitted from the synthetic recipe. Furthermore, we were already able to show that the replacement of the face-bridging azides by halides is possible from our results on an isostructural Mn<sub>18</sub>Dy (Dy<sup>III</sup> occupies the central Mn<sup>II</sup> position) complex in which six of the eight azides were replaced by chlorides.<sup>8</sup>

Here we describe the synthesis and magnetic characterisation of the coordination clusters [Mn<sub>19</sub>(O)<sub>8</sub>(HL<sup>Me</sup>)<sub>12</sub>( $\mu_3$ -Cl)<sub>6</sub>( $\mu_3$ OMe)<sub>2</sub>(MeOH)<sub>5</sub>(MeCN)<sub>6</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O·5MeOH·5MeCN (**2**) and [Mn<sub>19</sub>(O)<sub>8</sub>(HL<sup>Me</sup>)<sub>12</sub>( $\mu_3$ -Br)<sub>7</sub>( $\mu_3$ -OH)(MeCN)<sub>6</sub>]Br<sub>2</sub>·16H<sub>2</sub>O·11MeOH (**3**) in which the eight ( $\mu_3$ -N<sub>3</sub>) ligands in (**1**) have been replaced by either six ( $\mu_3$ -Cl) and two ( $\mu_3$ -OMe) (**2**) or by seven ( $\mu_3$ -Br) and one ( $\mu_3$ -OH) (**3**) (see Figure 1). We show that the ferromagnetic properties of **1** are unaffected by this change in the encapsulating ligand set in **2** and **3**. Density Functional Theory (DFT) calculations on **2** give a very similar picture of the magnetic interactions present here to those previously determined for **1**.<sup>4</sup> Furthermore, we show by electrospray mass spectrometry (ESI-MS) that the molecular structures of **1** and a related Mn<sub>18</sub>Y<sup>5</sup> complex are stable in other media.

Compounds **2** and **3** were obtained by reaction of H<sub>3</sub>L<sup>Me</sup> with MnCl<sub>2</sub>·4H<sub>2</sub>O (**2**) or MnBr<sub>2</sub>·4H<sub>2</sub>O (**3**) in the presence of Et<sub>3</sub>N in MeCN/MeOH mixtures and crystallised by slow evaporation of the mother liquor at room temperature. The synthesis of **2** and **3** was only possible at very dilute reactant concentrations and when Et<sub>3</sub>N was employed as base in place of NaOAc·3H<sub>2</sub>O, as observed in the synthesis of **1**.<sup>2</sup> Attempted direct substitution of the azides in **1** by reactions in MeOH with excess (Et<sub>4</sub>N)Cl or (Et<sub>4</sub>N)Br, as source of chloride or bromide, respectively, did not afford the desired compounds.

Single crystal X-ray analysis<sup>‡</sup> (Fig. 1) shows that **3** crystallises isotypical to **1** in *R*-3, whereas **2** crystallises in *P*-1 with *Z* = 1. However the difference is not that great since the triclinic crystal structure of **2** is in fact derived rather simply from the primitive rhombohedral lattice of **1** ( $a = 16.768$  Å,  $\alpha = 77.54^\circ$ ) by compression along the threefold axis and loss of the

threefold symmetry. Importantly, the cores of **2** and **3** are closely analogous to that of **1**, consisting of two supertetrahedral  $\{\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4\}$  units sharing a common  $\text{Mn}^{\text{II}}$  vertex.



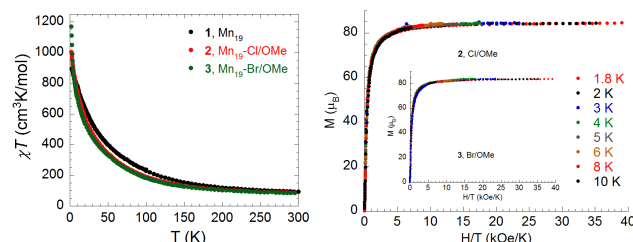
**Figure 1.** Molecular structures of the  $[\text{Mn}_{19}(\text{O})_8(\text{HL}^{\text{Me}})_{12}(\mu_3\text{-Cl})_6(\mu_3\text{-OMe})_2(\text{MeOH})_5(\text{MeCN})]^{2+}$  cluster in **2** (above) and the  $[\text{Mn}_{19}(\text{O})_8(\text{HL}^{\text{Me}})_{12}(\mu_3\text{-Br})_7(\mu_3\text{-OH})(\text{MeCN})_6]^{2+}$  cluster in **3** (below). Organic H atoms omitted for clarity. Colour code:  $\text{Mn}^{\text{III}}$  purple;  $\text{Mn}^{\text{II}}$  pale pink; O red; N blue; Cl green; Br orange.

Nonetheless, **2** and **3** differ from **1** in terms of their eight  $\mu_3$ -face-bridging ligands. In **2**, the two face-bridging ligands on the molecular threefold axis are both ( $\mu_3$ -OMe), while the remaining six are ( $\mu_3$ -Cl). Similarly in **3**, the two ligands on the threefold axis are a disordered combination of one ( $\mu_3$ -OH) and one ( $\mu_3$ -Br) while the remaining six are all bromides. We have previously observed ( $\mu_3$ -Cl) ligands in  $[\text{Mn}_{18}\text{Dy}]$ ,  $[\text{Mn}_{18}\text{Sr}]$ ,  $[\text{Mn}_{18}\text{Cd}]$ , and  $[\text{Mn}_{18}\text{Lu}]$  compounds and these compounds also feature disorder ( $\text{Cl}/\text{N}_3$ ) of the face-bridging ligands.<sup>8,9</sup> ( $\mu_3$ -Br) ligands such as those in **3** have been previously found on decanuclear supertetrahedral  $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4]$  clusters,<sup>10</sup> which have a structure corresponding to half of the  $\text{Mn}_{19}$  clusters **1**, **2** and **3**. Cluster **2** also differs from **1** and **3** in that its six terminal ligands on the outer  $\text{Mn}^{\text{II}}$  vertices of the supertetrahedron are five MeOH and one MeCN, instead of six MeCN.

The magnetic properties measured on polycrystalline samples of **2** and **3** show that the thermal evolution of the  $\chi T$  products are very similar to that of the original  $\text{Mn}_{19}$ -aggregate **1** (Fig. 2 left) with  $\chi T$  continuously increasing on lowering the temperature<sup>2</sup> and indicating that ferromagnetic interactions dominate. This is further confirmed by the field dependences of their magnetisation below 10 K, with the magnetisation saturating very fast and the reduced magnetisation curves at different temperatures superpose almost perfectly onto a master curve, indicating a lack of anisotropy (Fig. 2 right). The reduced magnetization curves of **2** and **3** could be reproduced with Brillouin functions calculated for  $S = 83/2$  and  $g = 2.02$  and  $2.03$  (Figs. S3) respectively, which are in very good agreement with those calculated for  $S = 83/2$  and  $g = 2.0$  as found for **1**.<sup>2</sup>

The high degree of similarity between the magnetic properties of **1**, **2** and **3** underlines the insensitivity to the nature of the face-bridging ligands, for which the simplest explanation is that these ligands are indeed relatively unimportant in the mediation of the ferromagnetic interactions, as indicated by DFT calculations.<sup>4</sup> To

confirm this, similar calculations were carried out on **2**. The exchange coupling constants  $J$  were calculated using the Heisenberg Hamiltonian<sup>4</sup> shown in the ESI (Table S2).



**Figure 2.** Temperature dependence of the  $\chi T$  products of **1-3** measured in  $H_{\text{dc}} = 0$  Oe,  $H_{\text{ac}} = 3$  Oe and  $\nu = 100$  or  $200$  Hz (left) and the reduced magnetisation ( $M$  -v-  $H/T$ ) curves for **2** and **3** (right).

From these studies, the calculated  $J$  values for **2** are generally found to be in agreement with those found from the previous calculations for **1**.<sup>4</sup> All interactions are calculated to be ferromagnetic with the exception of  $J_8$  ( $-0.2$   $\text{cm}^{-1}$ ), one of the three interactions involving the central  $\text{Mn}^{\text{II}}$ . The other two of these ( $J_6$  and  $J_7$ ) are also among the weakest of the observed ferromagnetic interactions. This observation, and/or the presence of very weak antiferromagnetic intermolecular coupling,<sup>2</sup> could explain why the maximum value of the  $\chi T$  at low temperatures is smaller than the expected one for a total spin ground state  $S = 83/2$ , but still higher than the expected for the spin inversion of the  $\text{Mn}^{\text{II}}$  cation ( $S = 73/2$ ).<sup>11</sup> The  $J_1$ - $J_5$  exchange interactions ( $\text{Mn}^{\text{III}}$ - $\text{Mn}^{\text{III}}$ ) are again, with the exception of  $J_4$ , the most ferromagnetic, and  $J_5$ , which involves interactions through both  $\mu_4$ -O and  $\mu_3$ -OMe bridging ligands, is the strongest.

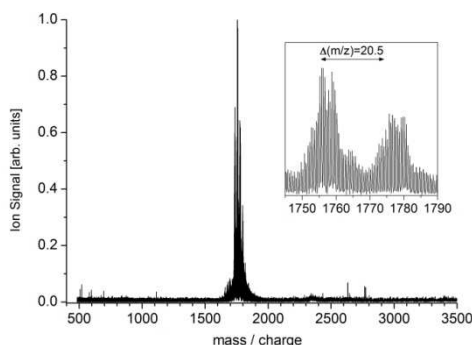
The similarities in the  $J$  values (particularly  $J_1$ - $J_5$ ) obtained for **2** and **1** confirm that the nature of the face-bridging ligand does not affect the character of those exchange interactions. This results from the fact that these  $\mu_3$ -ligands in each case coordinate on the significantly elongated Jahn-Teller axes of the  $\text{Mn}^{\text{III}}$  centres, such that they are unlikely to contribute significantly to the  $\text{Mn}^{\text{III}}$ - $\text{Mn}^{\text{III}}$  interactions. The ( $\mu_4$ -O) ligands, by contrast, all occupy equatorial sites on the  $\text{Mn}^{\text{III}}$  centres, and so constitute the dominant pathway for these interactions. By contrast, the replacement of  $\mu_4$ -OH ligands by  $\mu_4$ - $\text{N}_3$  bridges in a series of otherwise isostructural  $\text{M}^{\text{II}}_9$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Fe}$ ) clusters has been reported to result in changes in their magnetic properties.<sup>10</sup> In this case, however, the face-bridging ligands are more strongly bound than those in **1**, **2** and **3**.

Having established the magnetic robustness of **1** towards changes in the face-bridging ligands, our second goal was to investigate whether the molecule itself was robust in other media. The solid state (crystal structure and magnetism) characterisation of such cluster complexes gives no guarantee whether such species remain intact in other phases. For example, establishing stability in solution is imperative if studies of the clusters in biological media or on surfaces are to be meaningful. Furthermore, since studies of mixed-valence  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$  clusters on metal surfaces often show the formation of reduced cluster species,<sup>13</sup> it is also important to know that the original valence state can be maintained in other phases.

Our studies using electrospray-ionization mass spectrometry (ESI-MS)<sup>13,14</sup> to investigate the solution and fragmentation behaviour of the  $\text{Mn}_{19}$  aggregate **1** in MeOH and that of the related complex  $[\text{Mn}_{18}\text{Y}(\text{O})_8(\mu_3\text{-}\eta^1\text{-N}_3)_8(\text{HL}^{\text{Me}})_{12}(\text{MeCN})_6](\text{NO}_3)_3 \cdot 11\text{MeOH}$  (**4**) in 50:50  $\text{H}_2\text{O}$ -MeOH, which are relatively reactive solvents for such clusters, show that the clusters remain intact under these



conditions. The ESI-MS of compounds **1** (Fig. 3) and **4** (Fig. S6) each exhibit a single very narrow set of signals. For **1**, a dication centred at  $m/z$  1750.3 is observed, corresponding to  $[\text{Mn}_{19}\text{O}_8(\text{N}_3)_8(\text{HL}^{\text{Me}})_{12}]^{2+}$ , with weaker peaks centred at  $m/z$  1770.8, assigned to  $[\text{Mn}_{19}\text{O}_8(\text{N}_3)_8(\text{HL}^{\text{Me}})_{12}(\text{MeCN})]^{2+}$ . For **4** a trication centred at  $m/z$  1156.3 can be assigned to  $[\text{Mn}_{18}\text{YO}_8(\text{N}_3)_8(\text{HL}^{\text{Me}})_{12}]^{3+}$ . Remarkably, although they have lost their terminal ligands, both compounds fly without significant fragmentation. In particular, no signals corresponding to the cleaving of the clusters at the central metal could be observed. Furthermore, the overall charges on the clusters are maintained: for **4**, peaks corresponding to di- and tetracations were visible in the spectra, but with intensities well below 1% of the trication signals. Thus the structural integrity and the oxidation states of these two clusters are maintained both in solution and in the gas-phase.



**Fig. 3.** ESI mass spectra of **1** showing a group of peaks from a dication centred at  $m/z$  1750.3 and 1770.8.

In conclusion, we have synthesised and structurally characterised two new  $\text{Mn}_{19}$  aggregates, in which the  $\mu_3\text{-N}_3$  face-bridging ligands in the original  $\text{Mn}_{19}$  aggregate **1** have been replaced with either Cl and OMe, or Br and OH ligands. Magnetic studies show that the  $S = 83/2$  spin structure is stable to such changes. This had been theoretically predicted and has now been experimentally corroborated. This study confirms that the main mediators of the ferromagnetic coupling in the supertetrahedral subunits within the  $\text{Mn}_{19}$  system are the oxido bridges rather than the face-bridging ligands. In other words, in this case the inorganic  $\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8\}$  core of this coordination cluster system provides a remarkably stable unit in terms of its electronic structure and, apparently, in terms of the overall stability of the molecular system in various media such as in solution and in the gas-phase.

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#### Notes and references

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<sup>‡</sup> **2**:  $\text{C}_{132}\text{H}_{188}\text{Cl}_8\text{Mn}_{19}\text{N}_6\text{O}_{58}$ , 4114.34 g mol<sup>-1</sup>, triclinic, P-1,  $a = 14.1015(10)$ ,  $b = 16.5323(12)$ ,  $c = 18.1689(15)$  Å,  $\alpha = 93.821(6)$ ,  $\beta = 99.472(6)$ ,  $\gamma = 95.429(6)^\circ$ ,  $Z = 1$ ,  $V = 4144.6(5)$  Å<sup>3</sup>,  $T = 180(2)$  K,  $\rho_{\text{calc}} = 1.648$  g cm<sup>-3</sup>,  $F(000) = 2097$ ,  $\mu(\text{Mo-K}\alpha) = 1.603$  mm<sup>-1</sup>; 45111 data, 16961 unique ( $R_{\text{int}} = 0.0722$ ), 1030 parameters, final  $wR_2 = 0.1467$ ,  $S = 0.989$  (all data),  $R_1$  (10434 data with  $I > 2\sigma(I)$ ) = 0.0583. **3**:  $\text{C}_{131}\text{H}_{215}\text{Br}_9\text{Mn}_{19}\text{N}_6\text{O}_{72}$ , 4789.22 g mol<sup>-1</sup>, rhombohedral, R-3,  $a = 21.217(3)$ ,  $c = 35.704(5)$  Å,  $Z = 3$ ,  $V = 13919(4)$  Å<sup>3</sup>,  $T = 150(2)$  K,  $\rho_{\text{calc}} = 1.718$  g cm<sup>-3</sup>,  $F(000) = 7257$ ,  $\lambda = 0.8000$  Å,  $\mu = 4.368$  mm<sup>-1</sup>; 27023 data, 6425 unique ( $R_{\text{int}} = 0.0508$ ), 331 parameters, final  $wR_2 = 0.2040$ ,  $S = 1.099$  (all data),  $R_1$  (4639 data with  $I > 2\sigma(I)$ ) = 0.0644. CCDC 954052-954053.

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